Recovery of nutrients from biomass for nutrient recycling

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2013 Algae Biomass Summit

October 1, 2013
Background: Biomass at energy-consumption relevant scales exceeds current nutrient production

- To meet 10% of liquid fuel needs (roughly 30 BGY)
  - Algal biomass: 200 – 500 Mt/yr.
  - Nitrogen: 18 – 45 Mt/yr
    - Compare 14 Mt/yr in 2006
    - Haber-Bosch process requires energy.
  - Phosphorous: 2.4 – 6 Mt/yr
    - Compare 4.1 Mt/yr in 2006
    - P is mined resource.
    - Recent concerns over ‘peak phosphate:’

- Food vs fuel:
  - Nutrient use for algae should not compete with food production
  - Nutrient run-off has detrimental environmental consequences (algal blooms).

Need to recycle nutrients
Cannot afford to pass through once only

- Nutrients are needed for biological productivity, not fuel.
  - N: amino acids (incl. chlorophyll)
  - P: nucleic acids, phospholipids, ATP.

- Our work:
  - Develop and evaluate processes for nutrient recycling.
    - Two steps:
      - Convert organic N and P to inorganic forms.
      - Separate nutrients from energy products & return to culture.

- Target struvite (MgNH$_4$PO$_4$) as transportable, fungible nutrient.
  - Recovers 1:1 N:P
  - Precipitates at accessible concentrations.
    - Experience in waste water treatment industry.
  - Involves Mg readily available in seawater (and inexpensive otherwise).
  - Alternates include Ca and Mg phosphates.
Hypothetical process

1. **Cultivation**
2. **Harvest and dewater (>90% water)**
3. **Initial lipid extraction**
4. **Remineralize phosphate**
5. **Secondary lipid extraction**
6. **Protein fermentation**
7. **Struvite precipitation**

**Outputs:**
- **Lipids**
- **Butanol**

**Reagents:**
- Mg, PO$_4$
- MgNH$_4$PO$_4$
- NH$_3$
Remineralize phosphorous

- Remineralize P from organic phosphates (nucleic acids, ATP, phospholipids, luxury phosphate storage).

- **Approaches**
  - Dilute acid hydrolysis
  - Endogenous enzymes.
  - Supplemental enzymes.
  - See Todd Lane’s Wednesday afternoon talk.

- Results in PO4 availability in mM concentrations.
Remineralize N through protein fermentation

- Amino acid fermentation yields ammonium and higher alcohols.

- Proteins recalcitrant to dilute acid hydrolysis. Adding enzymemix more than doubles amino acid availability.

- Resulting ammonium available at moderate concentrations.
Hypothetical process

1. Cultivation
2. Harvest and dewater (>90% water)
3. Initial lipid extraction
   - Lipids
4. Remineralize phosphate
   - Mg, PO₄
   - MgNH₄PO₄
5. Secondary lipid extraction
   - Lipids
6. Protein fermentation
   - Butanol
7. Struvite precipitation
   - NH₃
Recover nutrients through precipitation

- Struvite (MgNH$_4$PO$_4$) is useful mineral form of nutrients.
  - Alternates include Ca and Mg phosphates.
  - Looking at designing system to maximize recovery – need to measure precipitation kinetics.

- At concentrations available in nutrient recovery, potential to recover >90% PO$_4^{-3}$.

- Outstanding issues with effect of organics on kinetics.
**Experiment Details:**
Struvite precipitated in situ in a Malvern Mastersizer
Particle size distributions measured via laser diffraction
pH range 8.7 – 8.85
Equimolar concentrations Mg, NH₄, and PO₄
Salts used → MgCl₂ • 6H₂O, KH₂PO₄, NH₄Cl
Total solution volume is 120 mL
pH adjusted using 1.0 M NaOH
Time started when pH rises above 8.0
Most results at 3000 rpm.

**Notes on the data:**
D[4,3] = Volume weighted mean
D[3,2] = Surface weighted mean
All diameters are in **microns**
Times are in **minutes**
Crystal size distribution is measured. pH is controlled within 8.5 < pH < 9.

Greater supersaturation yields greater mass precipitated.

Size distributions are similar even with very different total mass precipitated.

Supersaturation affecting nucleation more than size for this configuration.

$D_{4,3}$ = Volume weighted mean
$D_{3,2}$ = Surface weighted mean
Rate at which crystals form is strongly dependent on the salt concentration (supersaturation)

Low initial salt concentrations result in very slow crystal growth while higher concentrations result in greatly increased rates of precipitation
Predictions of reactant depletion using different reaction rate models (with lines) are compared with measurements (symbols) from (Kofina and Koutsoukos, 2005). (Nominally the two sets of symbols should follow the same trend: their spread is indicative of experimental uncertainty)
Mixing rates affect final size distribution

Need a good estimation for the actual shear rate in the geometries used to determine effects of shear on precipitation kinetics

Precipitation in a beaker using magnetic stir bar (much lower shear rate)
Hypothetical process

1. **Cultivation**
2. **Harvest and dewater (>90% water)**
3. **Initial lipid extraction**
4. **Remineralize phosphate**
5. **Secondary lipid extraction**
6. **Protein fermentation**
7. **Struvite precipitation**
8. **Lipids**
9. **Butanol**

- **Mg, PO_4**
- **MgNH_4PO_4**
- **NH_3**
Outdoor *N. salina* cultivation with struvite

- *Nannochloropsis salina* (CCMP 1776)
  - Control: seawater supplemented with ODI nutrients at a 16:1 N:P ratio
  - Struvite: commercial struvite to replace 33, 67 and 100% of the P.
  - Initial stocking density of ~0.15 g/L afdw at 5 cm depth
  - Water depth in each raceway was gradually increased to a final depth of 20 cm providing a total working volume of 550 L

**Daily biomass productivity (g AFDW/m²/day) cultivated with P replacement (% of control) using commercial struvite**
Cultivation with struvite (reagent grade and dairy-waste byproduct)

- Replace phosphate with struvite (reagent grade or dairy waste effluent product).
- With dairy waste effluent: remove trace metals and nutrients?
Cultivation with excess struvite

- Use enough struvite to provide recommended N, excess P (16x).
- 2/3 struvite does not initially dissolve (noisy absorption signal).
- Multicultivator, sinusoidal diurnal cycle, peak 1000°F, 21 to 24°C
Summary

• Production of algal biofuels at petroleum-replacement levels will involve substantial nutrients, impacting supplies unless recycling is implemented.

• Enhance biomass utilization
  • Remineralize P via acid hydrolysis or enzymatic processes.
  • Remineralize N in conjunction with protein fermentation.

• Recover nutrients through mineral precipitation, other separations.
  • Struvite is promising approach to recovery of P and fraction of N.
  • Measurements of size distribution evolution as function of reactant concentrations and mixing rates will guide process development.

• Cultivation using struvite is equivalent to that with original nutrients.
Acknowledgments

DOE EERE BioEnergy Technology Office

Sandia National Labs
- Ryan Davis
- Todd Lane
- Pamela Lane
- Nicholas Wyatt
- Deanna Curtis

Texas Agrilife
- Anthony Siccardi

Open Algae
- Peter Kipp
- Hoyt Thomas
THANK YOU

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Induction time shows a strong dependence on initial salt concentration (supersaturation) at low values and becomes relatively independent at high salt concentrations.
Algae cultivation and N:P ratios

- Traditionally: Redfield ratio (16:1 to 13:1) adopted for N:P ratio.
- Recent evidence suggests productive growth under range of N:P ratios
Nutrient costs are substantial

- Recent paper suggests nutrient costs (even with partial recycle) are substantial.